Combinatorial Measurements of Polymer Craze Growth Using the Copper Grid Test Method

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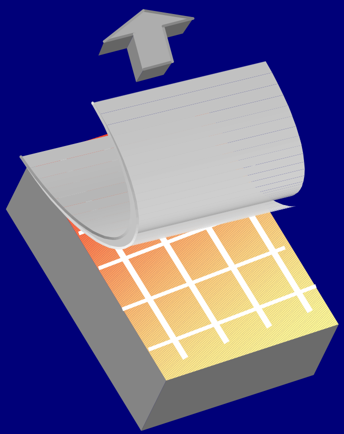
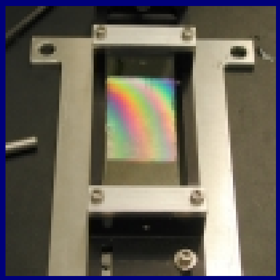
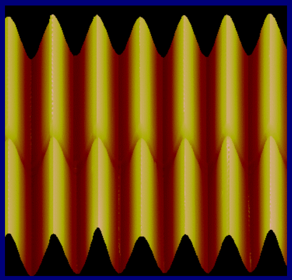
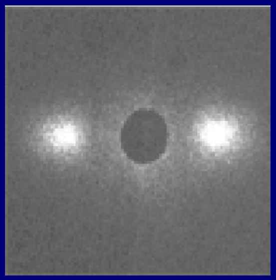
COMBI Crazing

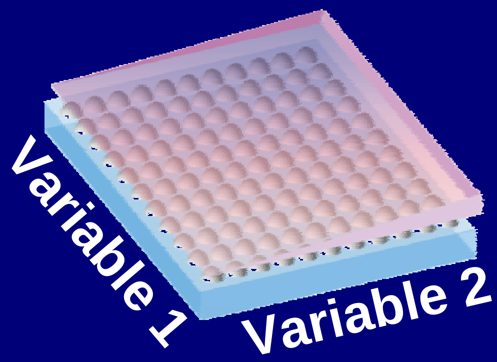
- COMBI thin films in the NCMC: gradients
- Polymer crystallization in thin films: iPS and PP
- Applying the Copper Grid Test to gradient thin films
- Composition gradients: filled polymer films
- Summary





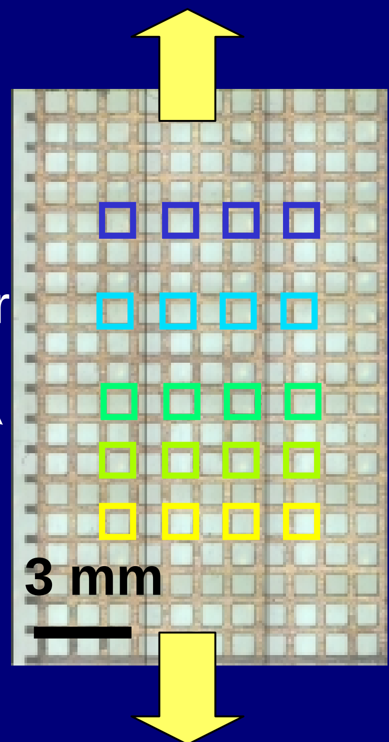






Copper Grid Tests and Gradient Thin Films

Copper Grid coated with glassy polymer



- Isolate crazes in thin films
  - Well suited to gradients
- *Statistical population of equally strained cells in one sample*
- Copper plastically deforms to "lock-in" applied strain
- *Use microscopy to analyze craze and fracture microstructures*

Lauterwasser, B.D. and E.J. Kramer. "Microscopic mechanisms and mechanics of craze growth and fracture", *Phil. Mag. A*, **39**, *4*, 469-495, 1979.

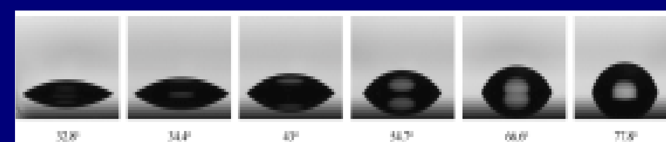
Combinatorial Approach to Polymer Films: Gradients

Variables:
- •Film thickness
- •Temperature
- •Crosslink density
- •Chemical functionality
- •Crystallinity
- •Composition
- •Surface Patterns

Properties:
- •Confinement
- •Surface energy
- •Adhesion energy
- •Toughness
- •Biocompatibility
- •Miscibility / Phase separation
- •Wettability

Polystyrene

h ~ 40 -120 nm

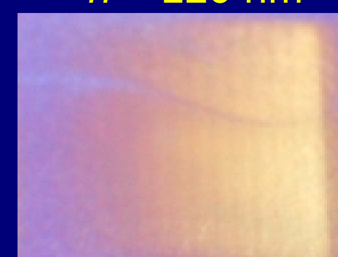


Poly(styrene-*b*-methyl methacrylate)

h ~ 40 -120 nm

Poly(vinyl cinnamate)

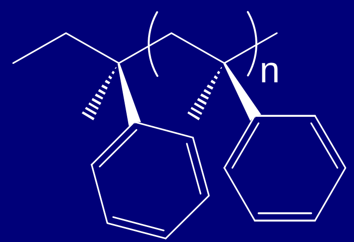
h ~ 120 nm



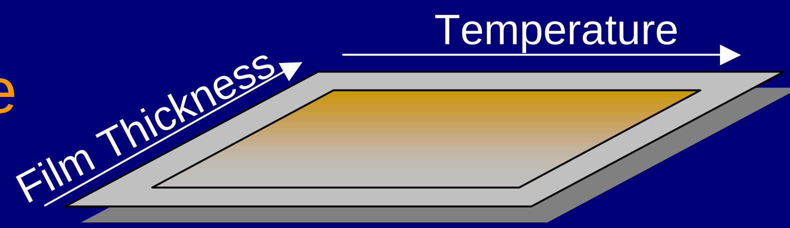
UV

Combinatorial / High-throughput Polymer Crystallization

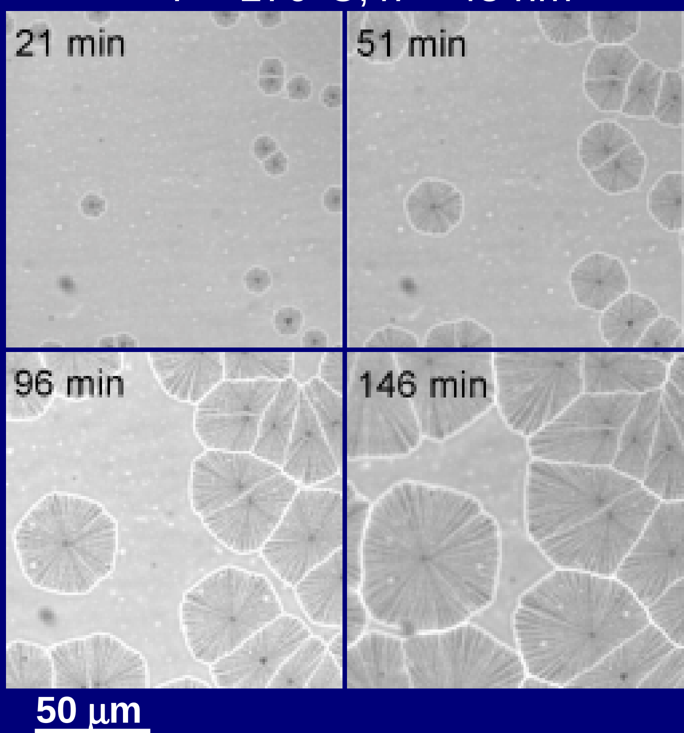
National Institute of Standards and Technology

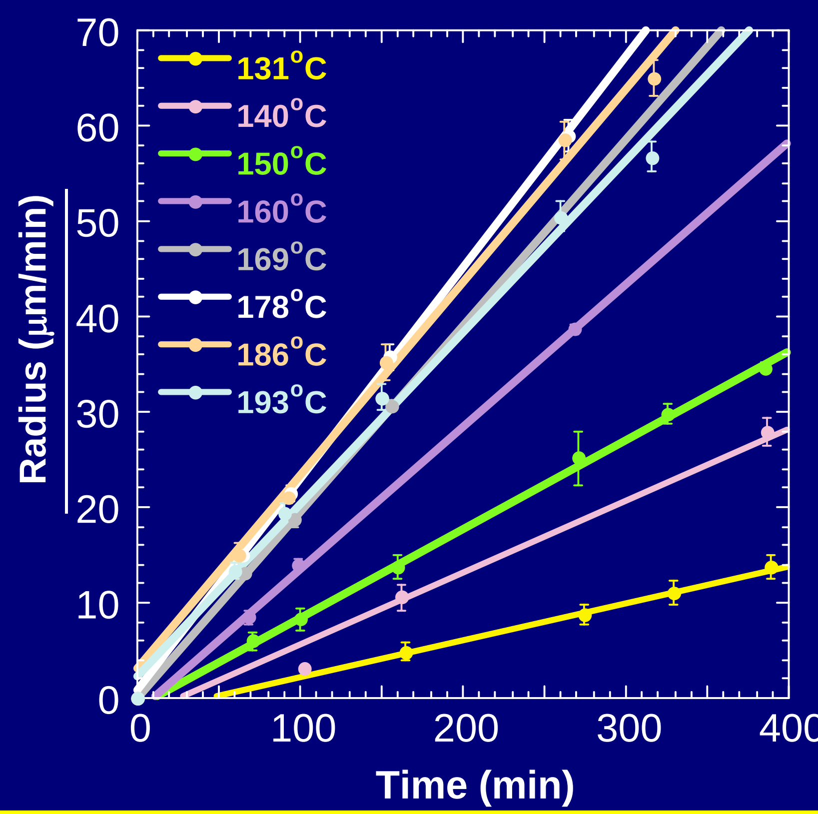


Isotactic Polystyrene

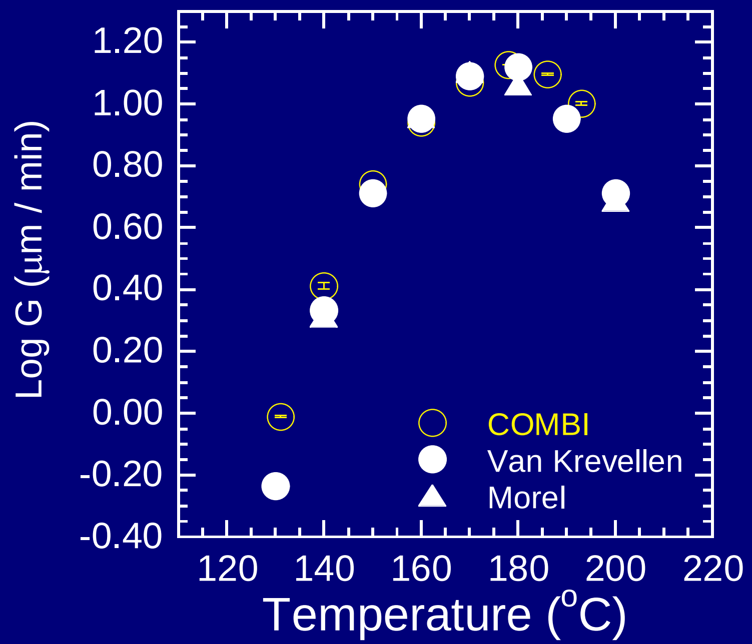


T = 170°C; *h* = 45 nm

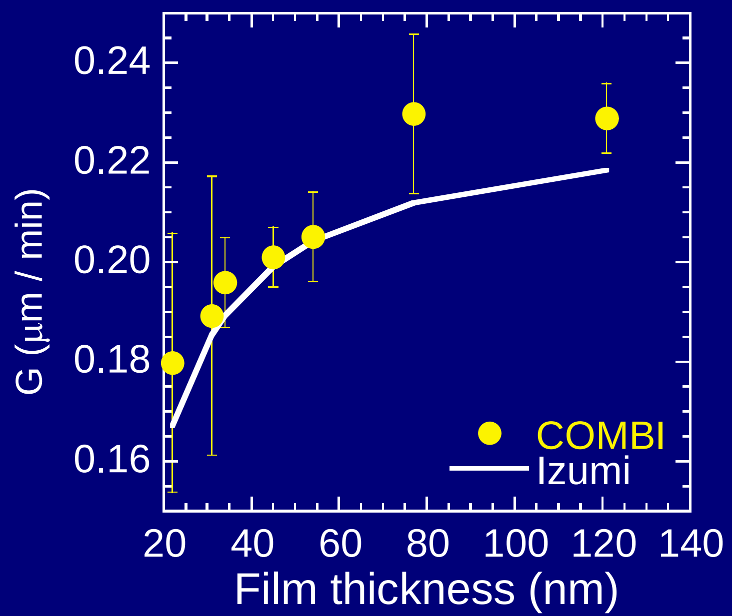




Crystallization Kinetics

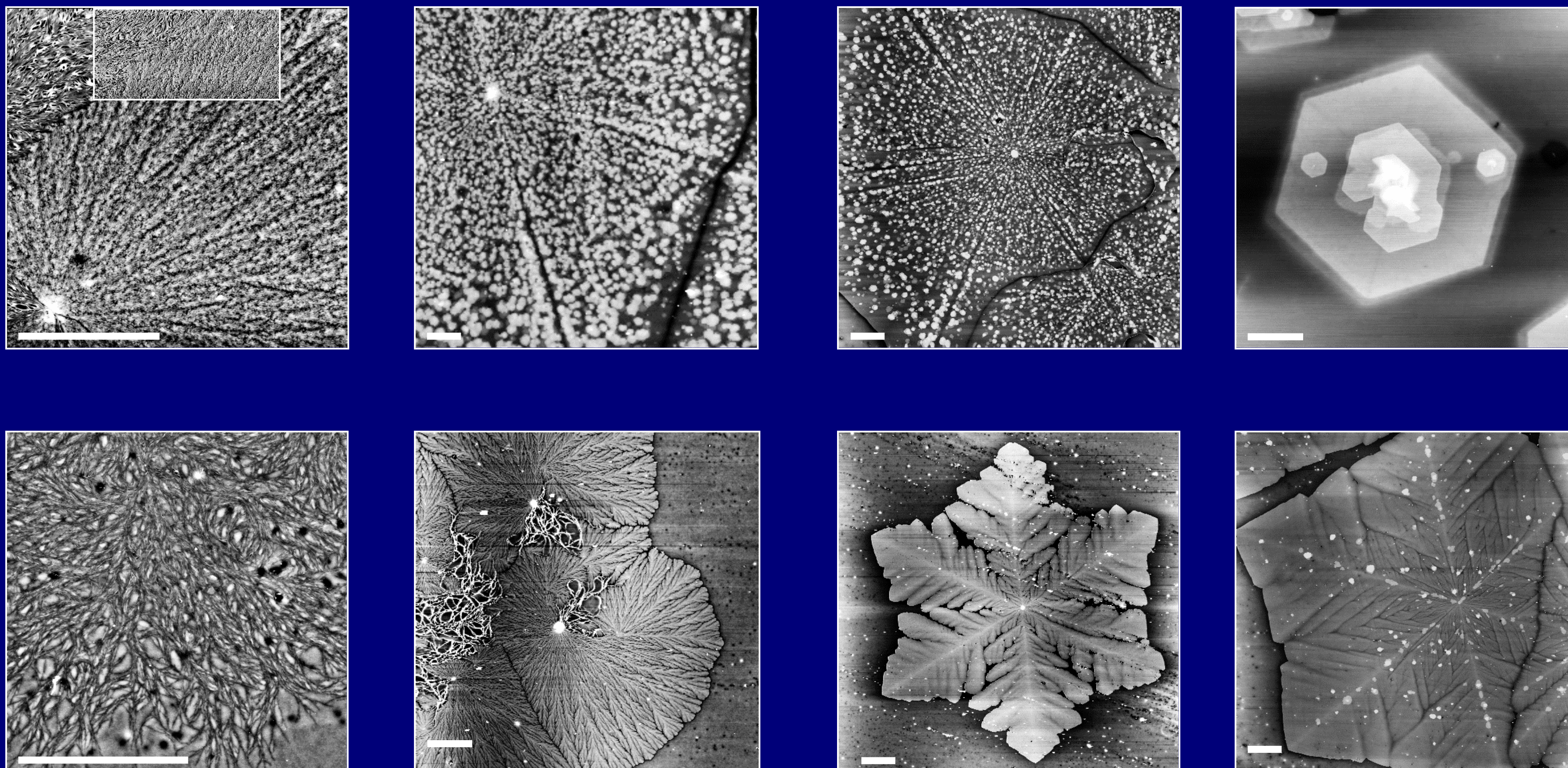


Viscoelastic effect:
As melt becomes more viscous, spherulites form and rates slow down.

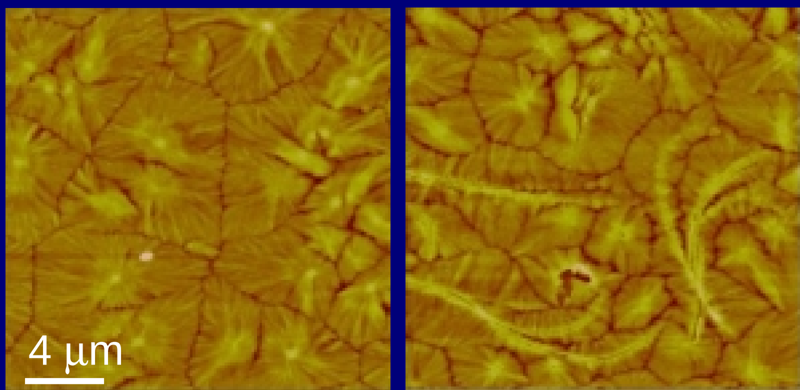


Surface tension anisotropy:
Decrease in rate is observed in blends and thinning films.

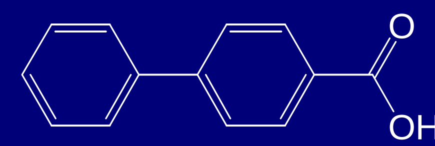
Crystallization Morphologies



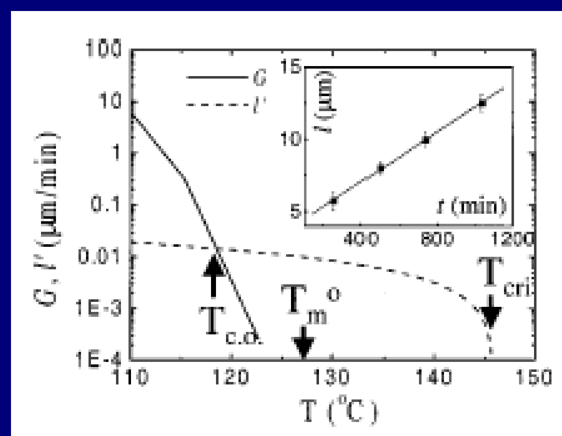
Polyolefin Crystallization Projects

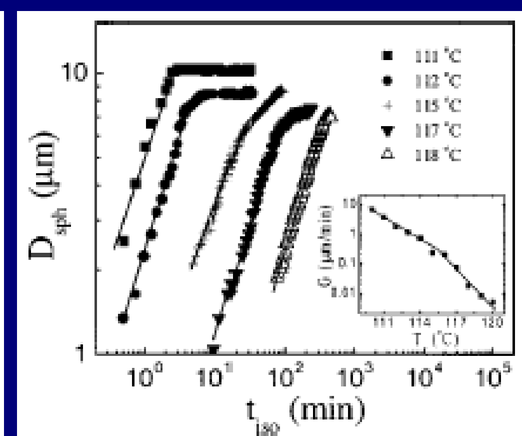


- Nucleating Agents in Polypropylene (M. Walker)
  – Temperature and composition gradients in the presence of 4-biphenyl carboxylic acid:



- Phase Separation vs. Crystallization (H. Wang)*
  – Poly(ethylene-*co*-hexene) / poly(ethylene-*co*-butene)
  – Temperature gradients





* Wang, H., Hobbie, E. K., Shimizu, K., Wang, G. Z. G., Kim, H. D. and Han, C. C., "*Competing Kinetics in Simultaneously Crystallizing and Phase-separating Polymer Blends*", ***J. Chem. Phys.*, 116,** 7311 (2002).

Combi Areas for Craze and Fracture Studies

NIST
National Institute of Standards and Technology

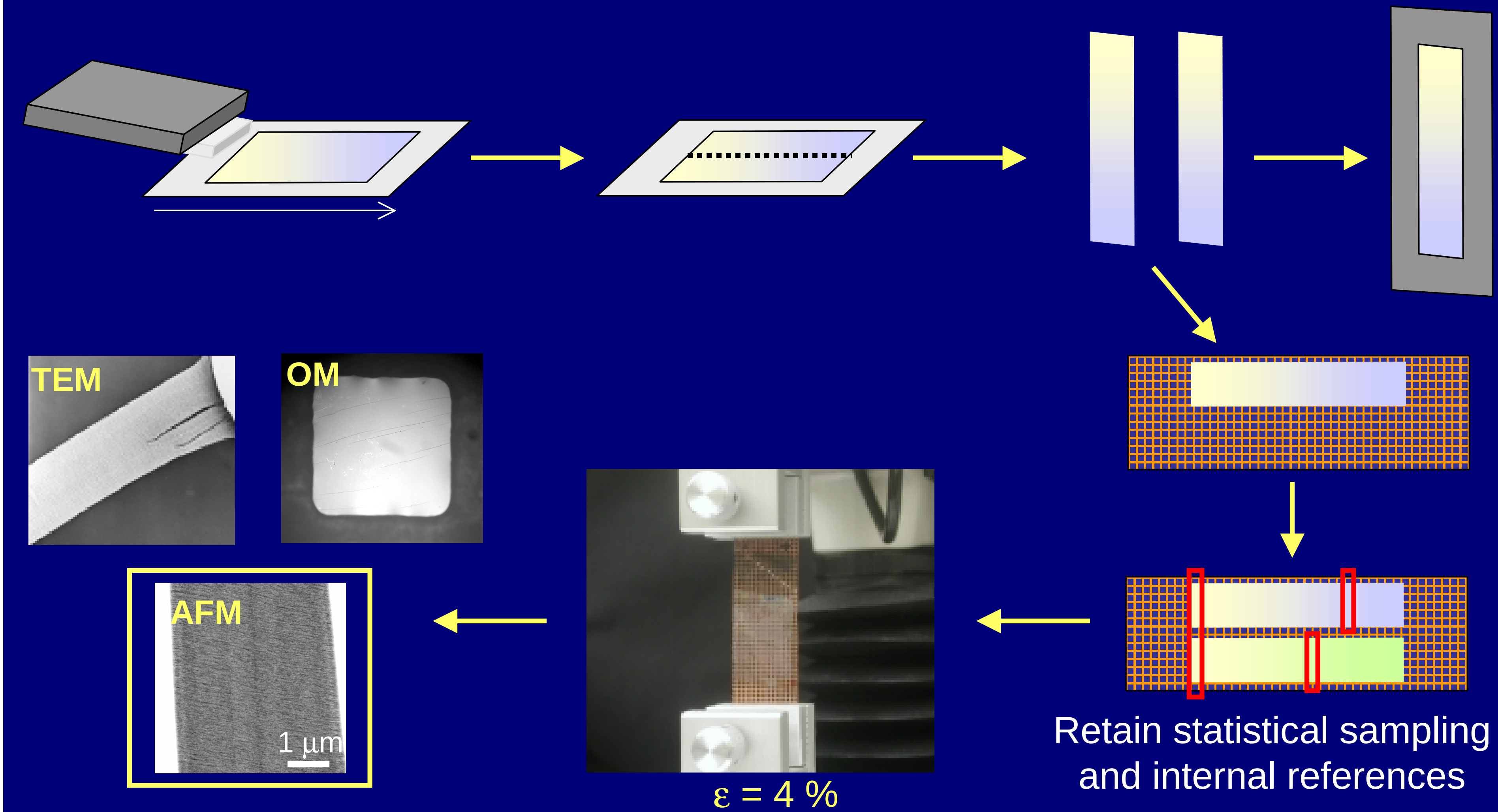
Materials Capabilities:

- *Thickness gradients*
  - *pS (tacticity)*
  - *pMMA*
- *Composition gradients*
  - *Silica particles in pS and pMMA matrices*
  - Polymer blends
  - Plasticized films
- Temperature gradients
  - Crystallinity
- Crosslink-density gradients

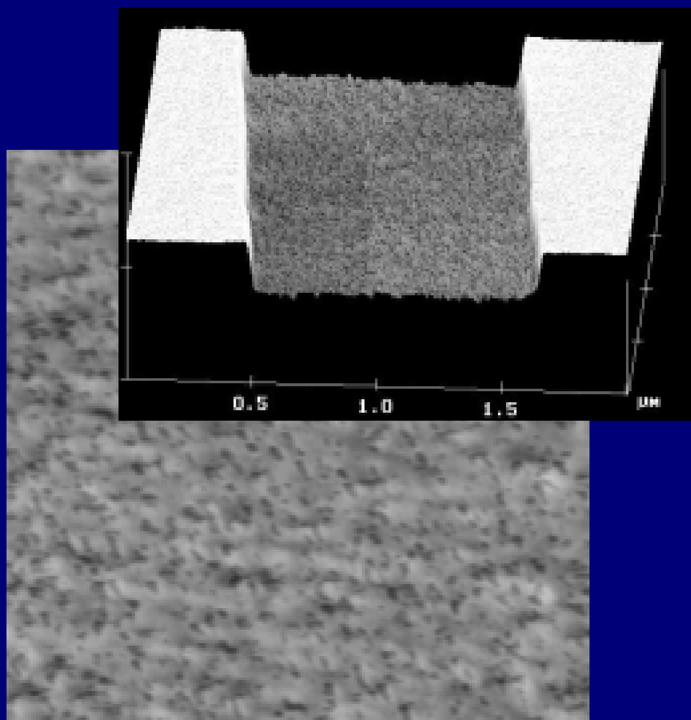
COMBI Tools:

- Flow coating / Interferometry
- Composition changes from continuous sampling
- *Image Analysis (IDL)*
  - *Fast and accurate*
  - *Consistent*
  - *New approaches to analysis!*
- Chemical mapping with IR Microscopy
- Automated, gradient UV exposure

Library Fabrication



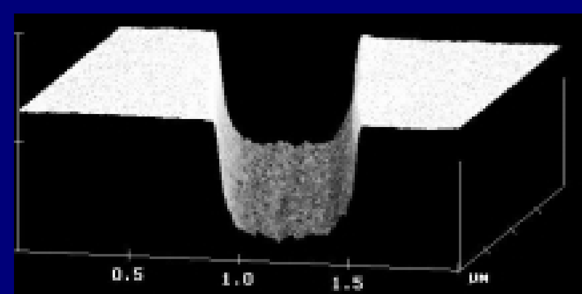
Validation: Polystyrene



250 nm

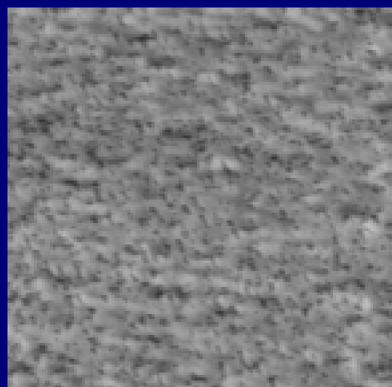
h = 78 nm

- Majority of literature: $h \geq 100$ nm
- Shoulder and neck regions in thicker films (mid-rib)
- Perforated microstructure in thin films (as opposed to discrete fibrils)

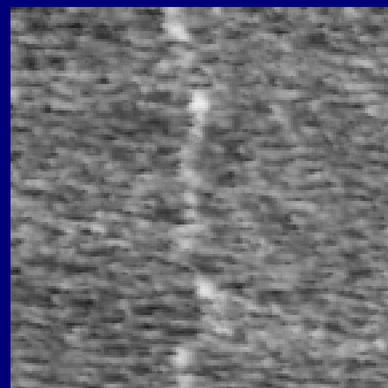


Microstructure & Film Thickness

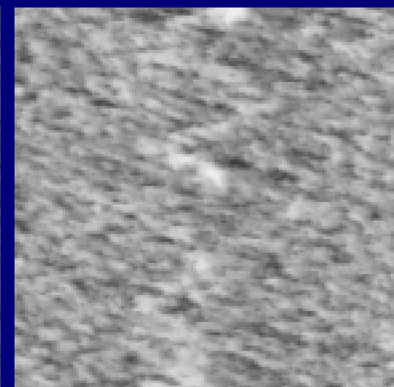
Atactic pS



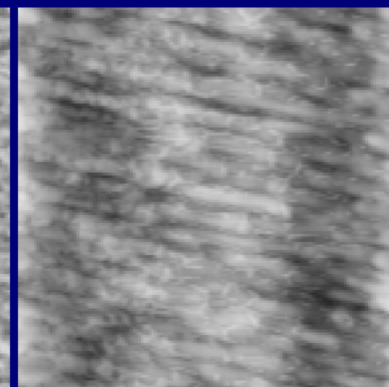
h = 78 nm



h = 100 nm

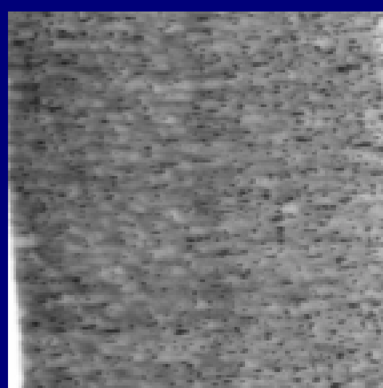


h = 112 nm

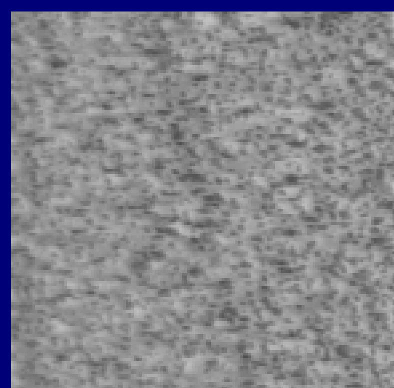


h = 190 nm

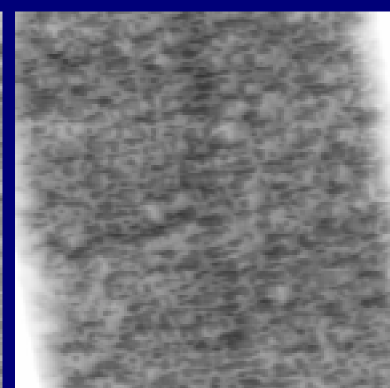
Isotactic pS



h = 77 nm



h = 103 nm



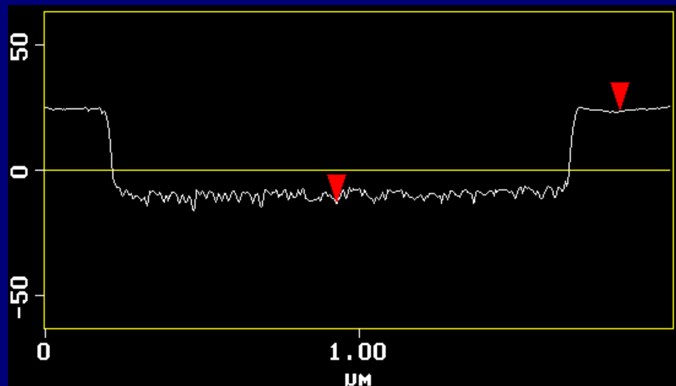
h = 115 nm

all images: 800 nm

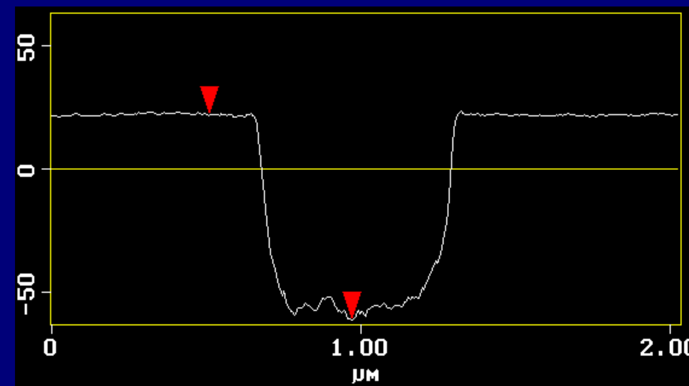
HT Image Analysis

National Institute of Standards and Technology

Manual Measurements:

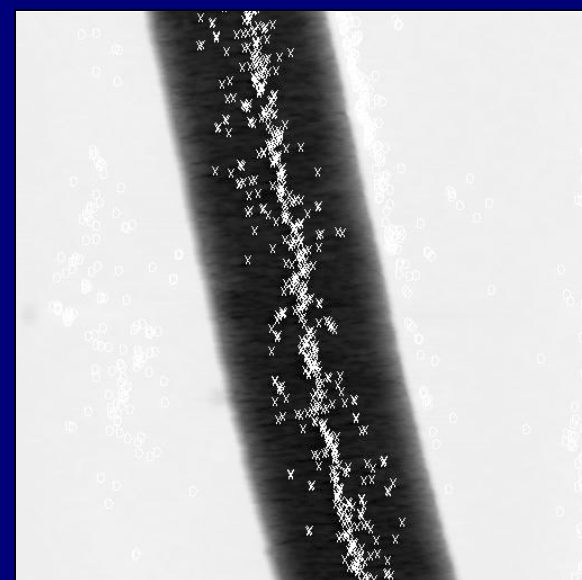


h = 78 nm

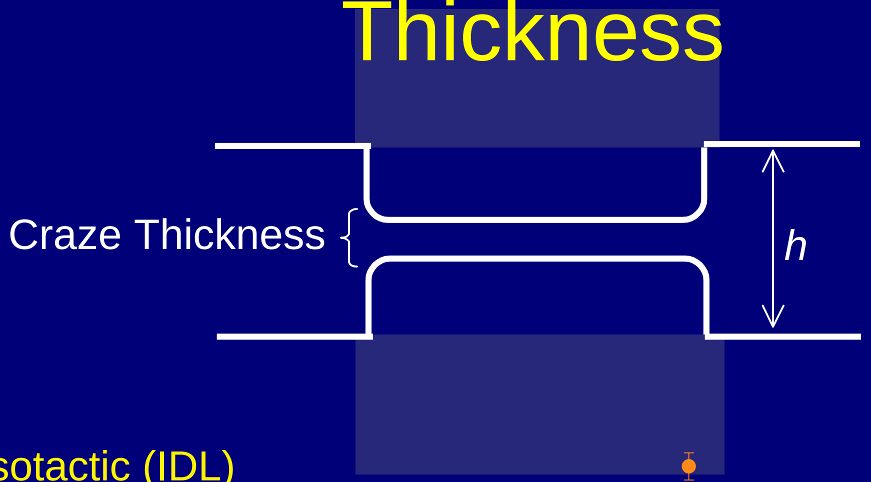


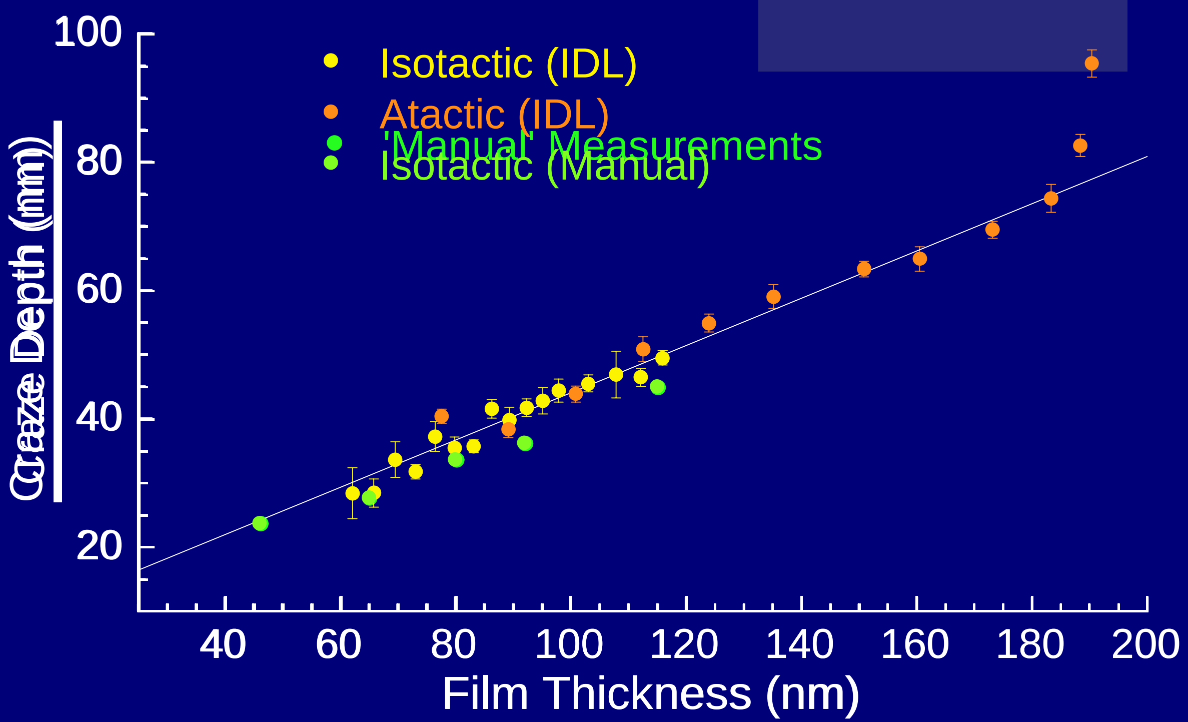
h = 190 nm

Automated Measurements:



Craze Depth vs. Film Thickness

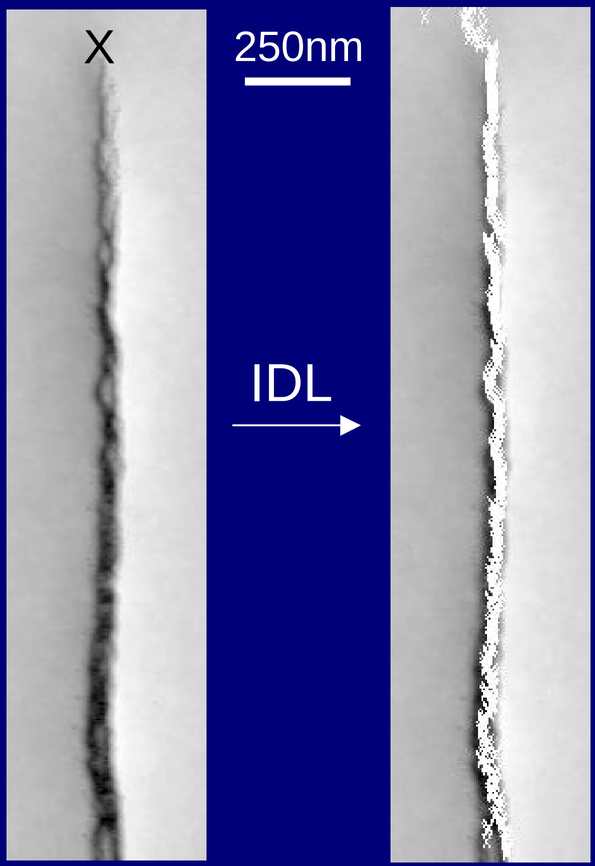




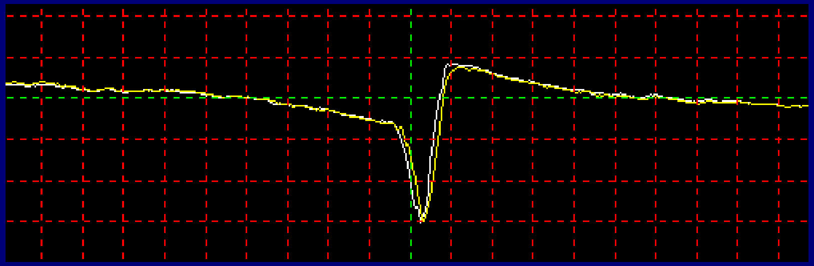
Craze Depth = 0.37*h*

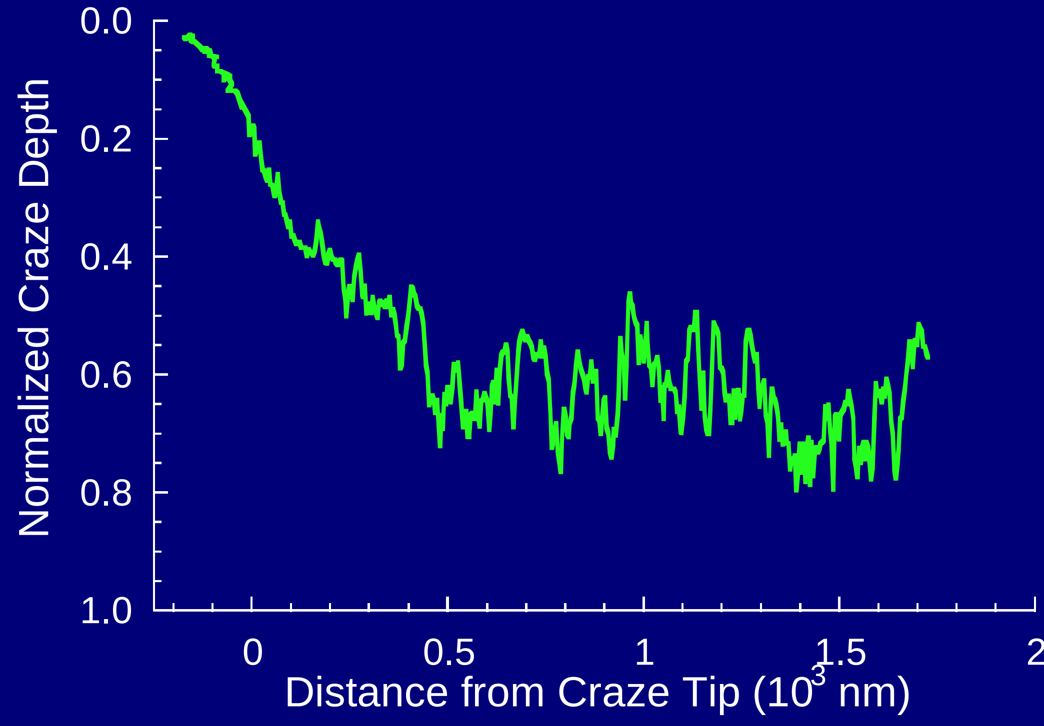
Craze Thickness = .26*h*

Craze Depth at the Crack Tip

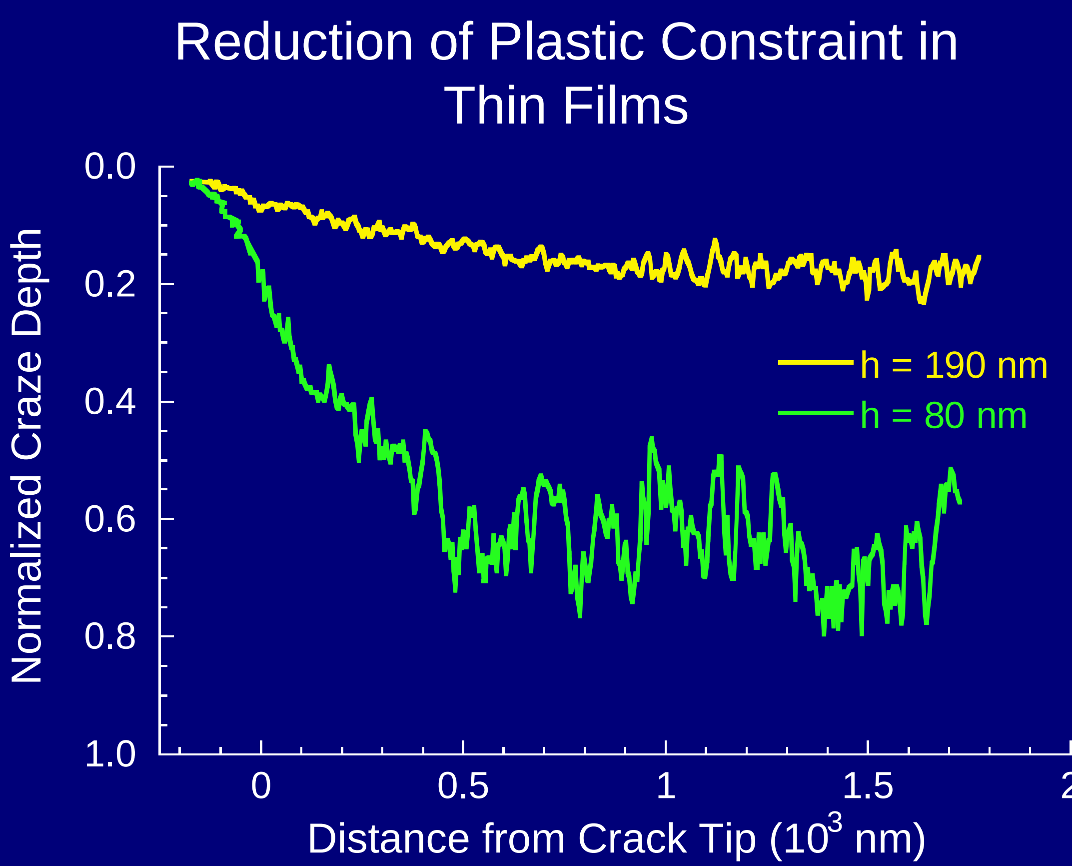


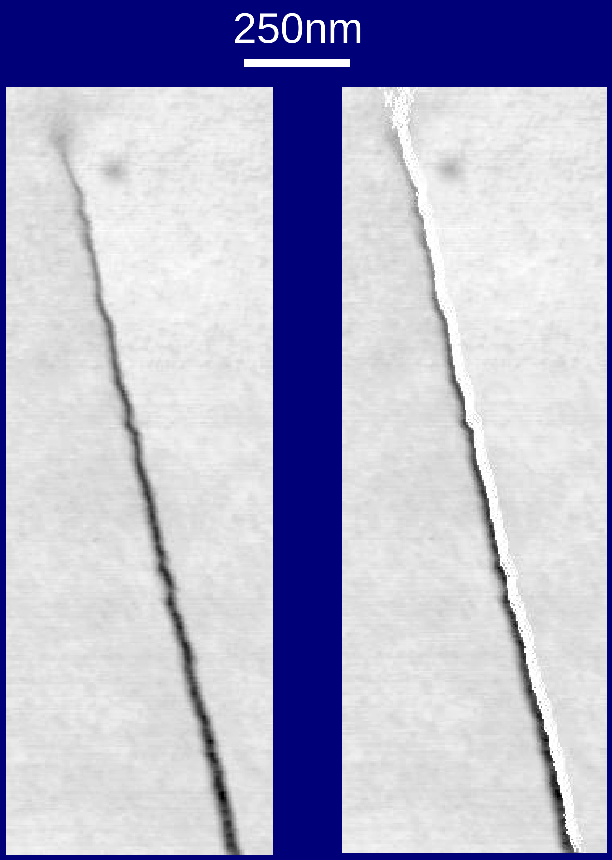
h = 80 nm





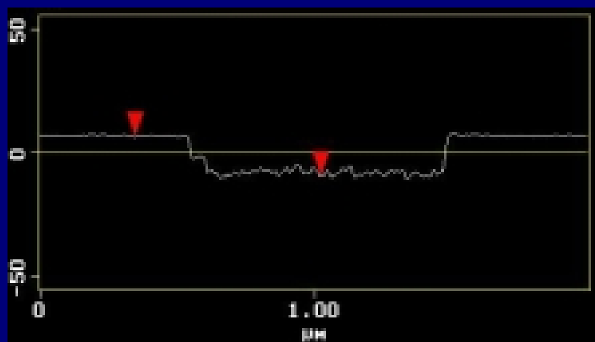
Craze Depth at the Crack Tip

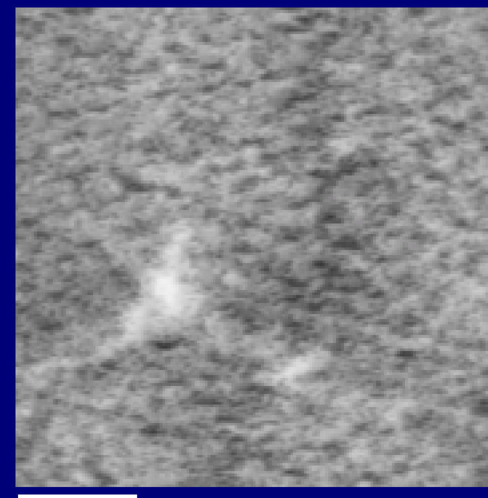


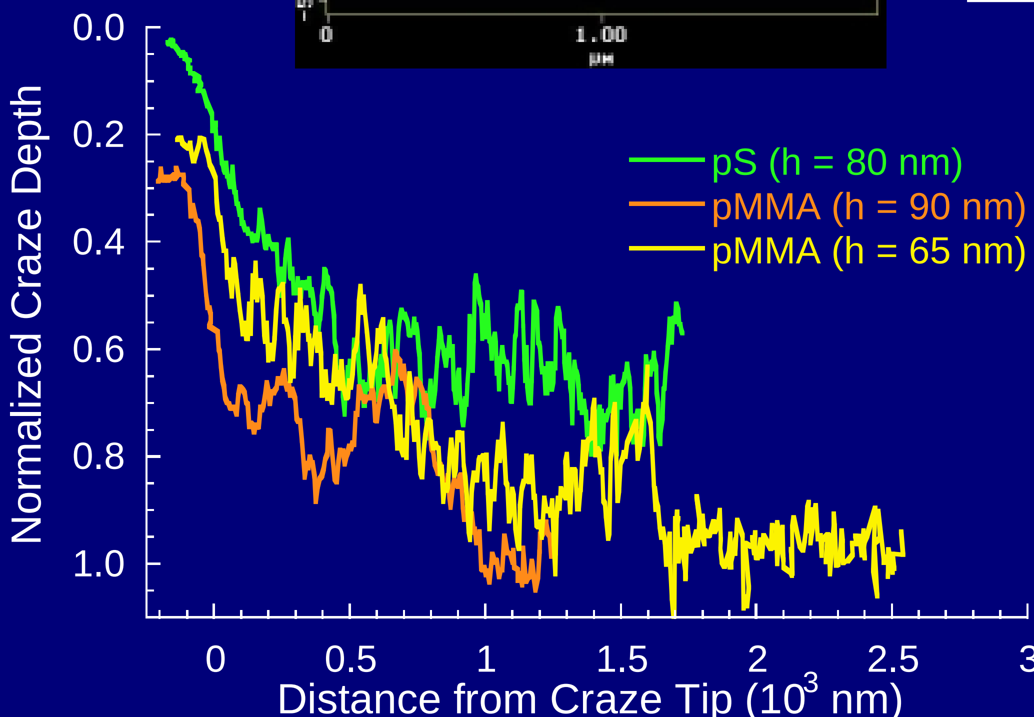


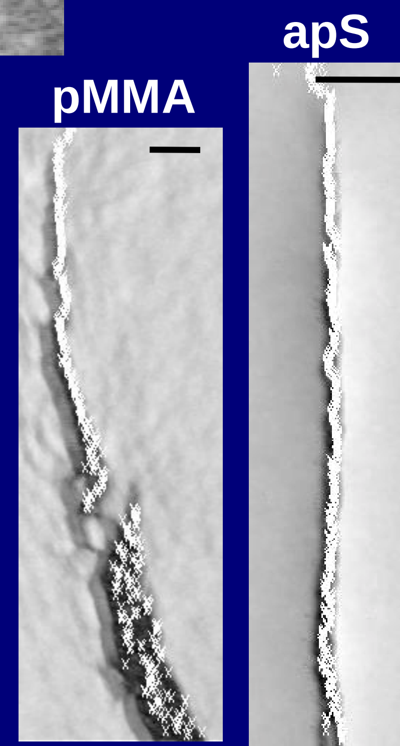
***h* = 190 nm**

pMMA



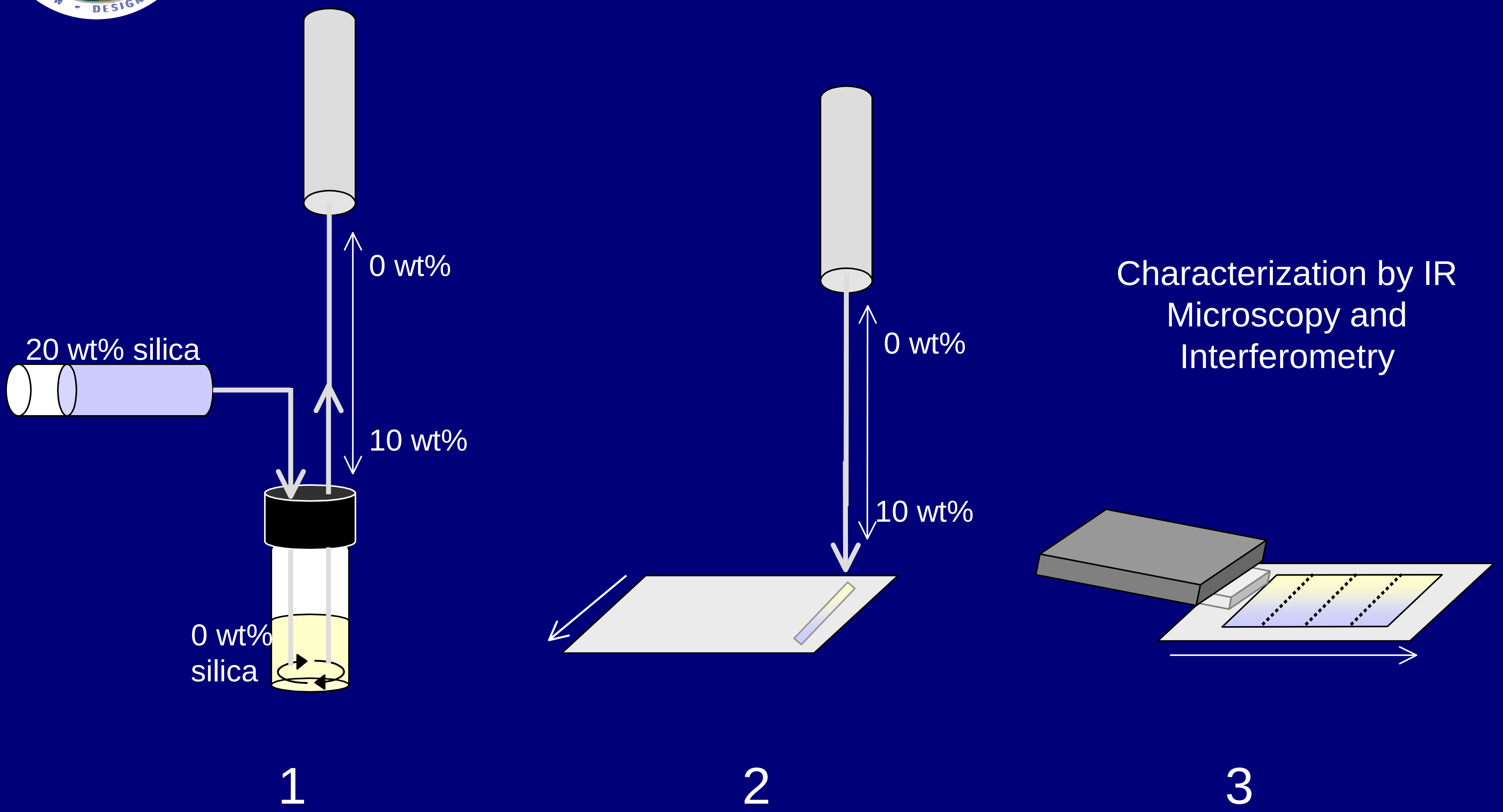




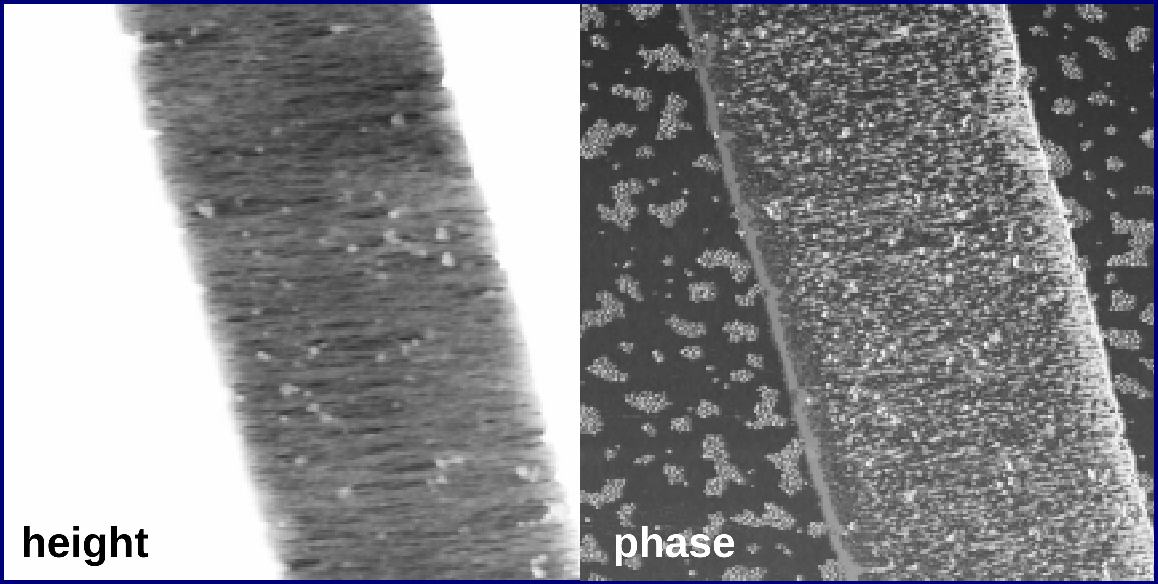


Scale bars: 250 nm

Filled Polymers: Composition Gradients



Filled Polymers: Composition Gradients



500 nm

Breakup of filler aggregates inside craze

Small voids induced in perforated microstructure by silica particles?

250 nm

Summary

- The Copper Grid Test method has been successfully adapted to a combinatorial and high throughput experiment using gradient film preparation methods and automated image analysis.
- Use of gradient films and automated image analysis not only accelerates the pace of experimentation, but reduces uncertainty, and can foster creative new ways of looking at experimental data.
- Future Directions:
  - Particle tracking during craze formation in filled polymers
  - Developing temperature and crystallinity gradients

Acknowledgments

Chris Stafford
Mike Fasolka
Marlon Walker